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COMPLETE SPECIFICATION

A process for the Production of Shaped Articles from Elastomeric Polymers containing Reactive Groups

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, of Leverkusen - Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of shaped articles from elastomeric polymers containing reactive groups.

It has been found that elastomeric shaped articles of high strength, such as for example filaments, films, foils or strips, can be obtained if a solution or emulsion of a synthetic elastomeric polymer containing reactive groups is introduced into a coagulating bath which contains an agent capable of reacting with the reactive groups to give cross-linking, for example a polyfunctional compound containing at least two groups which are capable of reacting with the reactive groups of the synthetic elastomeric polymer to give cross-linking, and the coagulate formed in the coagulating bath is removed from the bath and dried.

Suitable elastomeric polymers consist essentially of linear carbon chains to which are linked from 0.005—0.6 mols by weight per 100 parts by weight of elastomeric polymer of reactive groups such as carbonyl, carboxyl, sulphonic acid, amide or basic groups.

These polymers can be obtained by copoly-

merizing monomers which have polymerisable carbon-to-carbon double bonds and have an elasticising action with organic compounds which contain reactive groups and are copolymerisable with said elasticising monomers.

Examples of suitable monomers which have polymerisable carbon-to-carbon double bonds and have an elasticising action are acrylic or methacrylic esters of aliphatic alcohols with at least 4 C-atoms, preferably with 8—14 C-atoms, vinyl alkyl ethers the alkyl radical of which contains 1—8 C-atoms, and compounds with two conjugate carbon-to-carbon double bonds, such as for example butadiene or homologues and derivatives of butadiene, such as isoprene, 2:3-dimethyl butadiene, 2-chlorobutadiene and 2-cyanobutadiene. The said monomers which have an elasticising action are preferably used in proportions of 15—99 per cent. by weight calculated on the total amount of monomers used.

Examples of suitable copolymerisable compounds with reactive groups are those which contain carbonyl, carboxyl, sulphonic acid, amide or basic groups, preferably basic nitrogen groups, which are capable of salt formation with organic acids. Examples of polymerisable compounds containing carbonyl groups are: acrolein: α -substituted acroleins, such as α -methyl acrolein: vinyl alkyl ketones, such as for example vinyl methyl ketone, vinyl ethyl ketone and isopropenyl methyl ketone. Examples of polymerisable compounds with

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carboxyl groups are mono- and polycarboxylic α,β -ethylenically unsaturated acids, such as for example acrylic acid, methacrylic acid, sorbic acid, maleic acid, maleic acid anhydride or fumaric acid. It is also possible to use the mono-esters of the polycarboxylic acids, such as mono-esters of maleic acid with aliphatic, cycloaliphatic or araliphatic alcohols having 1—14 carbon atoms, as for instance maleic acid monomethyl ester, maleic acid monobutyl ester, maleic acid monododecyl ester and maleic acid monocyclohexyl ester. Examples of polymerisable compounds with amide groups are: acrylamide: α -methacrylamide: α -isopropylacrylamide: α -chloroacrylamide. Heterocyclic nitrogen bases containing vinyl groups such as 2-vinyl pyridine and 2-vinyl-5-ethyl pyridine are examples of basic unsaturated compounds. Vinyl sulphonic acid can if desired be used as a copolymerisable compound. Said monomers with reactive groups may be used in proportions of 0.5—50 per cent. by weight as calculated on the total amount of monomers.

In addition to the said monomers, other organic compounds each containing at least one polymerisable carbon-to-carbon double bond can be used for the production of the copolymers, examples of such compounds being styrene, acrylonitrile, methacrylonitrile, acrylic or methacrylic esters of alcohols with 1—3 C-atoms, vinyl chloride and 1,1-dichloroethylene.

Furthermore, polyfunctional monomers containing at least two active olefine double bonds which act as cross-linking agents can be used: however, these latter compounds should be used in comparatively small proportions, preferably not exceeding 0.001—1 per cent. by weight calculated on the total amount of monomers used. Examples of suitable cross-linking agents are aromatic hydrocarbons containing at least two vinyl groups such as divinylbenzene, esters of polyhydric alcohols or of aromatic compounds containing at least two phenolic hydroxy groups with α,β -ethylenically unsaturated monocarboxylic acids such as ethylene dimethacrylate, ethylene diacrylate, pentaerythrityl tetramethacrylate, resorcinol dimethacrylate, half-esters of maleic acid or substituted maleic acids such as α -chloro-maleic acid with polyhydric alcohols such as the reaction product of 1 mol of ethylene glycol or similar dihydric alcohols with 2 mols of maleic anhydride, the reaction product of trihydric alcohols such as trimethylol propane with two or three mols of maleic anhydride, and also divinyl ether and divinyl sulphone.

Other suitable copolymerisable compounds are those which have their reactive groups present in masked form, the said groups being liberated by reaction with a hydrolysing agent after the polymerisation: examples of such copolymerisable compounds are saponifiable esters, such as acrylic and meth-

acrylic alkyl esters, vinyl sulphonic alkyl esters, (e.g. butyl vinyl sulphonate) unsaturated nitriles (e.g. acrylonitrile) and the polymerisable amides referred to above.

Of the compounds with reactive groups referred to above, those which have proved particularly satisfactory are the polymerisable monomers containing carboxyl groups, since the copolymers obtained with these monomers produce shaped articles such as threads, or filaments of particularly high initial strength after coagulation.

For the production of shaped articles, the copolymers are preferably used in the form of their emulsions. The latter are obtained by emulsification of the monomers in accordance with known processes, preferably in an aqueous medium, and polymerisation in the presence of suitable catalysts.

Examples of emulsifiers are the alkali metal salts of paraffin sulphonates obtained by sulphochlorination of long-chained paraffins with 12—18 carbon atoms and subsequent saponification (German Patent 750,330). The polymerisation can be activated with free-radical-forming substances, such as for example azo dinitriles, per-compounds or redox systems. Particularly advantageous activators for the emulsions are aliphatic sulphinic acid salts, preferably with a carbon chain of 12—18 carbon atoms, without the addition of compounds yielding oxygen (Makromolekulare Chemie, Volume 3, page 43 (1949)). It is also possible to influence the thermoplastic behaviour of the copolymers by adding regulators. Prior to working up copolymers of butadienes, it is of course advisable to add stabilisers, such as for example phenyl- β -naphthylamine or suitable phenols. The copolymer emulsions can also be prepared by the monomers being polymerised in bulk form or in solution and being subsequently emulsified. The emulsions contain preferably 10—60 per cent. by weight of polymers. The polymers can alternatively be used in the dissolved form. Suitable solvents are aromatic hydrocarbons, such as benzene, chlorobenzene, 2,4-dichlorobenzene, ketones, such as methyl ethyl ketone, or mixtures of said solvents. The solution of the polymers in said solvents should contain 8—40, preferably 10—20, per cent. by weight of polymers.

The choice of the polyfunctional compounds which are to be reacted with the reactive groups of the copolymers is dependent on the nature of the reactive groups of the copolymers. Among the numerous combinations which are possible, polyfunctional compounds suitable for reaction with copolymers containing carbonyl groups include polyamines and polyamides containing at least two NH_2 groups, such as for example ethylene diamine, butylene diamine, hexamethylene diamine, nonamethylene diamine, diethylene triamine, triethylene tetramine, hexamethylene pentamine, hydrazine, urea, thiourea, oxalic acid

- diamide, succinic acid diamide, adipic acid diamide, and terephthalic acid diamide. In this case the carbonyl groups of the copolymers react with the amino groups with the formation of $>C=N$ linkages. For the copolymers containing carboxyl groups, examples of suitable polyamines are those containing at least two $N<R_1$ groups, R_1 and R_2 may be the same or different and each represents a hydrogen atom, an alkyl radical having 1—18 carbon atoms, an aryl radical such as the phenyl radical, or an aralkyl radical, such as a benzyl radical. Suitable polyamines are those referred to above by way of example: other suitable polyamines are those in which at least one hydrogen atom of one of the amino or imino groups is substituted by one of the aforementioned substituents, such as N - methyl-ethylene diamine, N,N'-dimethylethylene diamine and N, N,N' - N' - tetramethylethylene diamine. Furthermore, water-soluble salts or hydroxides of polyvalent metals, such as calcium chloride, barium chloride, magnesium chloride, zinc chloride, zinc sulphate, ferrous sulphate, barium hydroxide, calcium hydroxide, chromium acetate, chrome alum, copper acetate and aluminium salts such as aluminium sulphate can be used. The aforementioned cross-linking agents react with the carboxyl groups of the copolymers with the formation of salts, whereby said agents effect a cross-linkage of the copolymers by way of the salt groups formed. The polyamines can also be used in the form of their salts with weak organic and inorganic acids such as carbonic acid, acetic acid, benzoic acid, stearic acid and boric acid. If polyamines with primary or secondary amino groups or their salts are used as cross-linking agents the salt groups formed during reaction in the precipitating bath in the first stage are converted into amide or imide groups during the drying process which follows the coagulating step. Other suitable cross-linking agents are organic compounds containing at least two epoxy groups such as: diglycidyl trimethylolpropane, obtained by reaction of 1 mol of trimethylolpropane, with 2 mols of epichlorhydrin; diglycidyl - glycerin, obtained by reaction of 1 mol of glycerin with 2 mols of epichlorhydrin β,β - di(glycidyl-cxyphenyl)-propane, obtained by reacting 1 mol of di-p-hydroxyphenyl - dimethyl-methane with 2 mols of epichlorhydrin; diglycidyl-aniline. These polyepoxy compounds are preferably used in alcoholic solution. For accelerating the reaction of the epoxy groups with the carboxyl groups of the polymers, whereby polyester formation occurs, the polymer after leaving the coagulation bath can be after-treated with alkaline agents such as aqueous solutions of alkali metal hydroxides, alkaline earth metal hydroxides, ammonia, and organic amines such as dibutylamine, trimethylamine and triethylamine. The copolymers containing amide groups can be reacted with aliphatic and/or aromatic aldehydes such as acetaldehyde, propionaldehyde, butyraldehyde, glyoxal, benzaldehyde, preferably formaldehyde, its different polymeric modifications or compounds thereof yielding formaldehyde, such as hexamethylene tetramine, the sodium salt of α -hydroxy methane sulphinic acid, or compounds containing several reactive methylol groups, such as hexamethylol melamine or dimethylolurea. Polybasic organic acids, such as oxalic acid, itaconic acid, fumaric acid, maleic acid, succinic acid, glutaric acid, citric acid, adipic acid, tartaric acid, 1,5-naphthalene disulphonic acid and 1,3-benzenedisulphonic acid are suitable for reaction with the copolymers containing basic groups.
- As to the composition of the coagulating baths, preferably water or alcohols such as methanol, ethanol or mixtures of water with alcohols are used as solvents. The amount of cross-linking agent used can vary within wide limits. Preferably the proportion of a cross-linking agent should be sufficient to react with at least 1/10 of the reactive groups. Good results are also obtained if the amount of cross-linking agents is at least chemically equivalent to the reactive groups present in the polymers. For achieving this result the coagulating bath should preferably contain 1—50 per cent. by weight of cross-linking agent, although higher concentrations are also possible. Besides the cross-linking agents the coagulating bath can contain coagulating agents, for instance strong electrolytes such as sodium chloride, potassium chloride, sodium sulphate, calcium chloride, zinc chloride or magnesium chloride in amounts of 1—30 per cent. by weight. The pH value of the coagulating bath depends on the type of reaction by which cross-linking of the polymers takes place. When polymers with carboxylic or sulphonic acid groups are used, the pH value is preferably kept at 6—10 if polyamines and their salts and/or hydroxides of polyvalent metals are applied as cross-linking agents. The salts of the polyvalent metals call for a pH value of 4—7. With mixtures of polyvalent metal salts and polyamines the pH value can be kept at 6—10. For the coagulation of the polymers with carbonyl groups the coagulation bath should contain polyamines in the aforementioned concentrations, and the pH value of such coagulation baths should be kept at 7—10. When polymers with amide groups are used the coagulation bath contains aldehydes and may have a pH value of 6—10. The precipitation baths can also contain thickening agents, such as polyvinyl alcohol, salts of polyacrylic acid, alginate acid or carboxymethyl cellulose, which are soluble in water or alcohol, casein, gelatine or agar-agar in a concentration of 1—15 per cent. by weight. The temperature of the

coagulation bath depends on the reactivity of the components applied. Generally speaking the bath is kept at a temperature of 20—70° C.

- 5 After leaving the coagulation bath the coagulated articles can be washed with water or ethanol in order to remove any surplus of coagulating agents adhering to the coagulates. The temperature of the washing agents should be kept at 20—70° C. Finally the shaped coagulate is dried at a temperature suitably in the range 50—150° C., preferably 90—120° C.

- 15 The process is particularly suitable for the production of threads from aqueous emulsions of butadiene copolymers which contain carboxyl groups. These emulsions are introduced through a nozzle into the precipitating bath. By using polyvalent amines such as ethylene diamine, in the precipitating bath, which advantageously also contains electrolytes, such as for example calcium chloride or sodium phosphate, a thread which is ready for use is obtained immediately after the emulsion has entered the precipitating bath, it only being necessary for the said thread to be washed, dried and reeled. This thread shows excellent tensile strength values with high elongation only a short time after being dried, such as could not be formerly obtained with butadiene-containing polymers, even from solutions. It is obvious that the copolymer emulsions can have added thereto the conventional vulcanisation auxiliaries, such as sulphur and accelerators. The threads can also be heated to a temperature higher than that of the actual drying process, whereupon additional cross-linking may take place. Such after-treatments can also be carried out under tension or with additional shaping. The butadiene-acrylonitrile copolymers which contain free carboxyl groups present an excellent resistance to solvents and have a high tensile strength and a high resistance to ageing and heat.

- 45 The copolymer emulsions or solutions which have been described can of course also have added thereto other natural or synthetic rubber latices or plastic emulsions, fillers, plasticisers, resins, dyestuffs, pigments, solvents or other high polymers capable of being cross-linked in accordance with the same principle. Examples of such high polymers are polyacrylic acids, carboxymethyl cellulose, alginic acid, protein compounds such as casein; polyesters can also be used.

- 55 The mode of carrying out the present invention can be varied within very wide limits. Instead of producing threads, webs or films, it is for example also possible to produce hoses by the use of annular nozzles. Moreover, the working up and drying of the shaped coagulates which are obtained can be modified in practically any desired manner, it being of course always necessary to bear in mind the nature of the polymer to be used. Another

possibility is for textile filaments of natural or synthetic nature to be impregnated with the above-described polymer emulsions or solutions and introduced into a coagulation bath which contains suitable poly-functional compounds. Furthermore, textile threads can be extruded through a nozzle into the above-described coagulation bath simultaneously with the emulsion or solution, whereby threads or filaments with a core of textile fibres are obtained. The process can also be carried out by applying the latex or solution as a thin layer on to a firm surface, for example, a mould, metal plate or a rotating roller or introducing the latex or solution into a rotating mould and then if desired continuously coagulating and thereafter cross-linking it. Furthermore, leather, textile materials and paper fleeces can be impregnated by using an analogous method.

As already mentioned, the threads or moulded bodies produced by the present process show a surprisingly high strength shortly after entering the precipitation bath. This ensures that working up can be carried out satisfactorily. In addition, owing to the high strength of the threads which are obtained, a very high withdrawal speed is possible. Whereas according to processes hitherto known, withdrawal speeds of 1 metre per minute were achieved, the present process allows of using a withdrawal speed of 20—60 metres per minute. It is surprising that emulsions of comparatively low concentration containing 10—40 per cent. by weight of polymer can also be used for carrying out this process. It is of course also possible for the viscosity of the emulsions to be increased by suitable additives prior to preparation. The high strength also permits the production of very thin threads, having diameters of 0.06—0.2 mm, the preparation of which from emulsions formerly presented difficulties.

It is further to be emphasised that the vulcanisation which was formerly necessary can be dispensed with in connection with the polymers containing butadiene. In connection with the diene-free polymers, an increase in strength is produced by the process which is employed, the said increase being such as could otherwise only be obtained by complicated known after-treatment processes, for example with peroxides.

The following Examples, in which parts are by weight, further illustrate the invention.

EXAMPLE 1.

2200 Parts of butadiene, 1400 parts of acrylonitrile and 400 parts of the monobutyl ester of maleic acid are emulsified in 5,480 parts of a solution of 160 parts of the sodium salt of a paraffin sulphonic acid containing 12—18 carbon atoms in 5,360 parts of water and 120 parts of N-sulphuric acid and polymerised while stirring at 25° C. after adding 6.5 parts of diisopropyl xanthogen disulphide and

20 parts of the sodium salt of a paraffin sulphonic acid with 12—18 carbon atoms. 19.5 Parts of diisopropyl xanthogen disulphide are additionally added in three batches, each of 6.5 parts, when 25, 40 and 55% of the monomers have polymerised. After 26 hours, 80% of the monomers have polymerised. The reaction is stopped by adding 40 g. of sodium hydrosulphite, 3% (calculated on the monomers introduced) of the conventional stabilisers, such as phenyl- β -naphthylamine, are added and the mixture is degasified by steam distillation of the residual monomers. The emulsion obtained in this manner is extruded at a constant hydrostatic pressure in an upward direction through a nozzle into a solution of 350 parts of calcium chloride and 210 parts of ethylene diamine in 3500 parts of water at a temperature of 50° C. The thread which is formed is withdrawn over rollers, washed with water at a temperature of 50° C. and dried at 120° C. It is thereafter ready for use, shows a tensile strength of 1700 kg/cm² with a breaking elongation of 720% diameter of the thread (diameter=0.11 mm) and has an excellent resistance to solvents, to heat and ageing.

EXAMPLE 2.

1050 Parts of butadiene, 300 parts of styrene and 150 parts of maleic monobutyl ester are emulsified in 1895 parts of a solution of 60 parts of the sodium salt of a paraffin sulphonic acid containing 12—18 carbon atoms in 1850 parts of water and 45 parts of sulphuric acid and polymerised with the addition of 4 parts of diisopropyl xanthogen disulphide, as described in Example 1. With a polymerisation temperature of 35° C. a yield of 60% is obtained after 29 hours. The product is worked up as described in Example 1. When the emulsion is extruded through a nozzle into a solution of 350 parts of calcium chloride and 140 parts of triethylene tetramine in 3,500 parts of water at 65° C. a non-tacky thread which can be worked up satisfactorily and which has a high tensile strength after drying is immediately obtained. (Diameter of the thread 0.14 mm, tensile strength 1080 kg/cm², breaking elongation 700%).

EXAMPLE 3.

1950 Parts of butyl acrylate, 950 parts of 1,1-dichloroethylene and 150 parts of methacrylic acid are emulsified in 3260 parts of a solution of 105 parts of the sodium salt of a paraffin sulphonic acid containing 12—18 carbon atoms in 3200 parts of water and 60 parts of sulphuric acid, and polymerised while stirring with the addition of 22.5 parts of the sodium salt of a paraffin sulphonic acid with 12—18 carbon atoms at 25° C. A yield of substantially 100% is obtained after 4 hours. As described in Example 1, the emulsion thus obtained is extruded through a nozzle into a solution of 350 parts of calcium chloride and 175 parts of hexamethylene diamine in 3500 parts of water and a thread is

obtained which has good strength properties. (Diameter of the thread: 0.3 mm, tensile strength 220 kg/cm², breaking elongation 450%).

EXAMPLE 4.

1125 Parts of butyl acrylate, 225 parts of acrylonitrile and 150 parts of maleic acid monobutyl ester are emulsified and polymerised as described in Example 3. A yield of substantially 100% is obtained after three hours with a polymerisation temperature of 30° C. The emulsion is processed to form threads as described in Example 3.

EXAMPLE 5.

1200 Parts of butadiene, 150 parts of methyl methacrylate and 150 parts of maleic acid monobutyl ester are emulsified as described in Example 1 and polymerised at 40° C. with the addition of 5.4 parts of *n*-dodecyl mercaptan and 7.5 parts of the sodium salt of a paraffin sulphonic acid with 12—18 carbon atoms. After 15 hours the polymerisation is interrupted by the addition of 15 g of sodium hydrosulphite. Threads produced from the emulsion by the process described in Example 1 have a tensile strength of 660 kg/cm² and an elongation at break of 770% at a diameter of 0.25 mm.

EXAMPLE 6.

1275 Parts of butadiene 150 parts of acrylonitrile and 75 parts of methacrylic acid are emulsified and polymerised as described in Example 5. After 13 hours the polymerisation is stopped by the addition of 15 g of sodium hydrosulphite and the residual monomers are removed from the emulsion by steam distillation. By introducing the emulsion into a precipitation bath containing 120 parts of ethylene diamine and 300 parts of calcium chloride dissolved in 3500 cc. of water threads are obtained which, at a diameter of 0.18 mm, have a tensile strength of 491 kg/cm² and an elongation at break of 735%.

EXAMPLE 7.

5700 Parts of butadiene, 3500 parts of acrylonitrile and 800 parts of maleic acid monocyclohexyl ester are emulsified in 10,000 parts of water with the addition of 3500 parts of a 10% solution of the sodium salt of a paraffin sulphonic acid with 12—18 carbon atoms and 300 parts of N sulphuric acid. Polymerisation is initiated by forcing in an aqueous solution of 50 g of the sodium salt of a paraffin sulphonic acid with 12—18 carbon atoms. As regulator, 40 g of diisopropyl xanthogen disulphide are added under pressure in three portions after 15, 30 and 45% of the monomers have polymerised. A yield of 77% polymer is obtained at a temperature of 25° C. after 25.5 hours. The polymerisation is stopped by the addition of 100 g of sodium hydrosulphite dissolved in 2000 cc. of water and the resulting mixture is degasified as described in the preceding Examples. Threads produced from this emul-

sion have a tensile strength of 1270 kg/cm² and an elongation at a break of 660% at a diameter of 0.14 mm.

EXAMPLE 8.

- 5 6500 Parts of butadiene, 2500 parts of methyl methacrylate and 1000 parts of maleic acid monocyclohexyl ester are emulsified and polymerised as described in Example 7. At a temperature of 35° C. a yield of 72% is
10 obtained after 32 hours. The threads produced from this emulsion have a tensile strength of 570 kg/cm² and an elongation at break of 720% at a diameter of 0.22 mm.

EXAMPLE 9.

- 15 3000 Parts of butadiene, 2500 parts of acrylonitrile, 3500 parts of methyl methacrylate and 1000 parts of maleic acid monobutyl ester are emulsified and polymerised as described in Example 7. At a polymerisation

temperature of 45° C. a yield of 75% is obtained after 35 hours. The thread produced from this emulsion is extraordinarily resistant to heat and ageing and, after heating to 140° C. for 30 hours, has a tensile strength of 446 kg/cm² and an elongation at break of 375%.

EXAMPLES 10—17.

7000 Parts of butadiene, 1000 parts of acrylonitrile, 1250 parts of styrene, 500 parts of maleic acid monobutyl ester and 250 parts of methacrylic acid are emulsified and polymerised as described in Example 7. At a polymerisation temperature of 20° C. a yield of 81% is obtained in 17.5 hours.

The emulsion thus prepared is coagulated in different coagulating baths. The composition of these baths and the physical data of the threads prepared from this emulsion under the conditions set forth are given in the table below:

40 Example No.	10	11	12	13	14	15	16	17
water, cc.	3500	3500	3500	3500	3500	—	—	3500
ethyl alcohol, cc	—	—	—	—	—	3500	3500	—
calcium chloride, g.	350	—	—	—	300	240	240	—
barium chloride, g.	—	250	—	—	—	—	—	—
45 barium hydroxide, g.	—	110	—	—	—	—	—	—
copper acetate, g.	—	—	250	—	—	—	—	—
zinc acetate, g.	—	—	—	250	—	—	—	—
calcium acetate, g.	—	—	—	—	—	—	—	250
ethylene diamine g.	115	—	100	110	—	130	—	120
50 triethylene tetra-amine, g.	—	—	—	—	105	—	—	—
glycerine diepoxide, g.	—	—	—	—	—	—	210	—
Tensile strength, kg/cm ²	960	210	432	362	782	695	215	562
55 Elongation at break, per cent.	680	820	580	630	620	540	470	710

The glycerine diepoxide was produced by the process disclosed in U.S. Specification No. 2,581,464. It had a chlorine content of 8.7%, a molar weight of 330 and contained per 149 g one mol by weight of epoxide.

EXAMPLE 18.

- 7000 Parts of butadiene, 2500 parts of acrylonitrile and 500 parts of vinyl methyl ketone are emulsified in 10,800 parts of water with the addition of 2000 parts of a 10% solution of the sodium salt of a paraffin sulphonic acid containing 12—18 carbon atoms and 200 parts of N-sulphuric acid. The polymerisation is initiated by the addition of 40 parts of the sodium salt of a paraffin sulphonic acid containing 12 to 18 carbon atoms. 30 Parts of *n*-dodecyl mercaptan are added in two portions during polymerisation to control the polymerisation process. At a polymerisation temperature of 25° C. a yield of 82% is obtained in 32 hours. The polymerisation

is interrupted by the addition of 30 g of hydroquinone and the latex stabilised with 3% by weight of phenyl- β -naphthylamine referred to the monomers used. The emulsion is then freed of its residual monomers by steam distillation and extruded through a nozzle into a solution of 180 parts of ethylene diamine and 320 parts of calcium chloride in 3500 parts of water at 50° C. The thread thus formed is withdrawn over rollers washed and dried. It has a tensile strength of 375 kg/cm² and an elongation at break of 520%.

EXAMPLE 19.

7000 Parts of butadiene, 2500 parts of acrylonitrile and 500 parts of α -methyl acrolein are emulsified and polymerised as described in Example 19. The degasified emulsion is extruded through a slot-shaped nozzle into a solution of 125 parts of ethylene diamine and 370 parts of calcium chloride in 3500 parts of water, and the coagulation sheet

thus formed is withdrawn over rollers, washed at 50° C. and dried at 110° C. The resulting rubber sheet has a tensile strength of 215 kg/cm² and an elongation at break of 450% at a thickness of 0.2 mm.

EXAMPLE 20.

2100 Parts by weight of butyl acrylate and 900 parts by weight of methyl methacrylate are emulsified in 3700 parts by weight of a solution of 110 parts by weight of the sodium salt of a paraffin sulphonic acid containing 12—18 carbon atoms in 3200 parts by weight of water and 60 parts by weight of N-sulphuric acid and polymerised with the addition of 22.5 parts by weight of the sodium salt of a paraffin sulphonic acid containing 12—18 carbon atoms at 30° C. while stirring. After 6 hours a yield of almost 100% is obtained.

5000 Parts by weight of this emulsion are slowly mixed while stirring with 1400 parts by weight of a 10% aqueous caustic soda solution and stirred at 50° C. for 5 hours. The emulsion is then mixed while stirring with 100 parts by weight of a polyglycol ether of lauryl alcohol and acidified with dilute sulphuric acid to pH 4. By extruding this emulsion through a nozzle into a solution of 150 parts by weight of ethylene diamine and 350 parts by weight of calcium chloride in 3500 parts by weight of water, a thread is obtained which is resistant to ageing.

What we claim is:—

1. A process for the production of shaped articles, which comprises introducing a solution or emulsion of a synthetic elastomeric polymer containing reactive groups into a coagulating bath which contains an agent capable of reacting with the reactive groups to give cross-linking, removing the coagulate formed in the coagulating bath from the bath and drying the coagulate.

2. A process as claimed in claim 1, wherein the reactive groups of the synthetic elastomeric polymer are carbonyl, carboxyl, sulphonic acid, amide or basic nitrogen groups.

3. A process as claimed in claim 1 or 2, wherein the cross-linking agent in the coagulating bath is a polyamine, a polyepoxy compound, a water-soluble salt of a polyvalent metal, a water-soluble hydroxide of a polyvalent metal, an aldehyde, a polycarboxylic acid or an organic polysulphonic acid.

4. A process as claimed in any of Claims 1—3, wherein the synthetic elastomeric polymer consists essentially of a linear carbon chain to which are linked from 0.005—0.6 mols by weight of reactive groups per 100 parts by weight of polymer.

5. A process as claimed in any of claims 2—4, wherein the synthetic elastomeric polymer is obtained by copolymerising in aqueous emulsion a monomer which has at least one polymerisable carbon-to-carbon double bond and has an elasticising action with a copolymerisable ethylenically unsaturated organic compound containing as reactive groups carbonyl, carboxyl, sulphonic acid, amide or basic nitrogen groups.

6. A process as claimed in any of Claims 1—5, wherein the coagulating bath contains an electrolyte having a coagulating action in addition to the component which causes cross-linking.

7. A process as claimed in any of Claims 1—6, wherein the polymer is extruded through a nozzle into the coagulating bath.

8. A process as claimed in any of Claims 1—6, wherein the polymer is introduced into the coagulating bath while in contact with a firm support.

9. A process for the production of shaped articles substantially as described with reference to any of the Examples.

10. Shaped articles whenever produced by the process claimed in any of the preceding claims.

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